THE ROLE OF AQUEOUS THIN FILM EVAPORATIVE COOLING ON RATES OF ELEMENTAL MERCURY AIR-WATER EXCHANGE UNDER TEMPERATURE DISEQUILIBRIUM CONDITIONS

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Abstract. Numerous technical studies have demonstrated that vapor phase air-water exchange of a number of toxicants including elemental mercury display a diel cycle. Specifically, daytime rates of air-water exchange can exceed nighttime values by 33 to 300% (e.g. see references cited in Loux, 2000 and Loux, 2001). Loux (2001) illustrated that while diel water column elemental mercury concentration cycles may tend to be the dominant factor in observed diel cycles in elemental mercury air-water exchange rates, the effect of diel cycles in temperature disequilibrium between the atmosphere and underlying waters also may be significant.

One issue not addressed in the previous work is the effect of evaporative cooling on the transport properties of the thin diffusive aqueous layer dominating air-water elemental mercury exchange. Specifically, because the diffusivity of heat in water may exceed molecular diffusivity by a factor of 100 (Jahne et al., 1987), it has been previously assumed that the temperature of the thin aqueous film equals the atmospheric value. The present work is designed to assess the significance of evaporative cooling on diel elemental mercury air-water exchange rates.

Utilizing procedures designed to relate atmospheric wet bulb temperatures to atmospheric relative humidities and dry bulb temperatures, the significance of the likely maximum effect of evaporative cooling on air-water elemental mercury exchange is estimated to be less than the significance of both diel cycles in water column elemental mercury concentrations and diel cycles in air water temperature disequilibria.

INTRODUCTION

Rates of vapor phase toxicant exchange between the atmosphere and underlying waters under quiescent conditions can be estimated using the two layer model (for gases in general: Lewis and Whitman, 1924; Liss and Slater, 1974; for elemental mercury: Schroeder et al., 1992; Loux, 2000; and Loux, 2001):

$$\text{Flux} = \frac{C_{atm.} - HC_{aq.}}{1/k_{atm.} + H/k_{aq.}}$$

where

Flux = rate of air-water exch. (ng/m^2hr)
$C_{atm.}$ = atmospheric Hg^o conc. (ng/m^3)
$C_{aq.}$ = water column Hg^o conc. (ng/m^3)
H = Henry's law constant (dim'less)
$k_{atm.}$ = atm. mass transfer coeff. (m/hr)
$k_{aq.}$ = aq. mass transfer coeff. (m/hr)

Using the 20 °C elemental mercury mass transfer coefficients published by Shroeder et al. (1992) and previously published expressions for estimating atmospheric partial pressures and aqueous solubilities of elemental mercury under variable temperature conditions, Loux (2000) extended the two layer model in two ways: 1) non-isothermal Henry's Law constants were developed to account for the effects of the diel air-water temperature disequilibrium conditions likely to be found in the environment, and 2) the aqueous phase mass transfer coefficient at 20 °C was extended to other aqueous thin film temperatures by incorporating the effects of temperature-sensitive aqueous viscosities. Loux (2001) further extended the approach to examine a diel scenario of variable water column dissolved gaseous mercury concentrations by fitting a fifth order polynomial to data that was published by Krabbenhoft et al. (1998) from the Florida Everglades. Using representative environmental conditions, Loux (2001) concluded: 1) diel air-water temperature disequilibria could significantly perturb diel elemental mercury air-water exchange rates, and 2) variations in diel elemental dissolved gaseous mercury

concentrations were likely more significant to variations in diel exchange rates than diel air-water temperature disequilibria. These findings were predicated on the assumption that the temperature of the aqueous thin film dominating rates of air-water elemental mercury exchange equaled the atmospheric temperature. The present effort is designed to assess the potential maximum effects of evaporative cooling on diel exchange rates by utilizing available relationships among atmospheric dry bulb thermometer temperatures, relative humidities and atmospheric wet bulb temperatures.

METHODS

The psychrometric equation (e.g, Martinez, 1994) relates atmospheric dry bulb and wet bulb temperatures (T_{dry} and T_{wet}) to percent relative humidity (RH) by:

$$\varepsilon_{wet} - \varepsilon_{dry}*RH/100 = K*p*(T_{dry} - T_{wet})$$

where ε_{wet} is the atmospheric water vapor saturation partial pressure at T_{wet}, ε_{dry} is the atmospheric water vapor saturation partial pressure at T_{dry}, "p" is the atmospheric pressure and K is the psychrometric constant (6.53E-4; Martinez, 1994). As noted by Martinez (1994), there is no explicit algebraic relationship for estimating T_{wet} from T_{dry} and RH; hence iterative solutions using estimates of water vapor partial pressures must be utilized. Martinez (1994) published vapor pressure expressions derived both from the Clausius-Clapeyron equation and from a polynomial fit to vapor pressure data. In this work, the temperatures of the aqueous thin film regulating air-water elemental mercury exchange will be assumed to equal either the atmospheric dry bulb or the atmospheric wet bulb temperatures estimated using Martinez's expressions.

All of the assumptions given by Loux (2001) will be utilized in the following simulations with the following additions/exceptions: 1) the atmospheric pressure will be assumed to remain constant at 0.101 MPa, 2) the atmospheric water vapor concentration will remain constant in the temperature range 20-30 °C–corresponding to 70% RH at 25 °C (e.g., see the March data for Miami Florida at http://water.dnr.stat.sc.us/climate/sercc/products/normals/085658_30yr_norm. html) and 3) the temperature of the thin aqueous film regulating elemental mercury air-water exchange will be assigned both atmospheric dry and wet bulb temperature values.

RESULTS

Given a constant atmospheric water vapor partial pressure corresponding to 70% RH at 25 °C, the estimated RH values at 20 and 30 °C are estimated to be 95% and 52.3% respectively. Using the iterative procedure described by Martinez (1994), the following wet bulb temperature depression values (dT; i.e., $dT = [T_{dry} - T_{wet}]$) are estimated to be: $dT = 0.55$ °C at $T_{atm} = 20$ °C, $dT = 3.93$ °C at $T_{atm} = 25$ °C, and $dT = 7.36$ °C at $T_{atm} = 30$ °C. These values are consistent with estimates derived from a table published by Lutkens and Tarbuck (1986).

Figure 1 illustrates the findings obtained under 24 hour simulation scenarios using both wet and dry bulb temperatures for the temperature of the thin aqueous film regulating air-water elemental mercury exchange. The two curves in the 2 to 3 unit range represent the dry bulb and wet bulb atmospheric temperature values (divided by 10) as a function of time of day. Note that the wet bulb temperature (the lower curve) approaches the dry bulb temperature (the upper curve) when atmospheric temperature approaches 20 °C (i.e., when the relative humidity approaches 100%).

The remaining two curves in Figure 1 illustrate predicted evasion rates when the aqueous thin film temperature is assumed to equal the atmospheric dry bulb temperature (the upper curve) and the aqueous thin film temperature is assumed to equal the atmospheric wet bulb temperature (the lower curve). Note that when the RH approaches 100% (during hours 4 to 6), both approaches yield comparable estimated exchange rates. Only during the period of the maximum atmospheric temperature (hours 13 to 16) do the two exchange estimates significantly differ; this difference can be attributed to evaporative cooling.

CONCLUSIONS

Based on the findings from earlier work (Loux, 2001) and the present study, those variables governing diel elemental mercury air-water exchange rates in environmental systems are likely to fall into the following order of significance: diel water column dissolved gaseous mercury concentrations > diel air-water temperature disequilibria > diel evaporative cooling of the thin aqueous layer dominating air-water elemental mercury exchange.

The wet bulb temperature values used in these simulations are likely to contain maximum differences

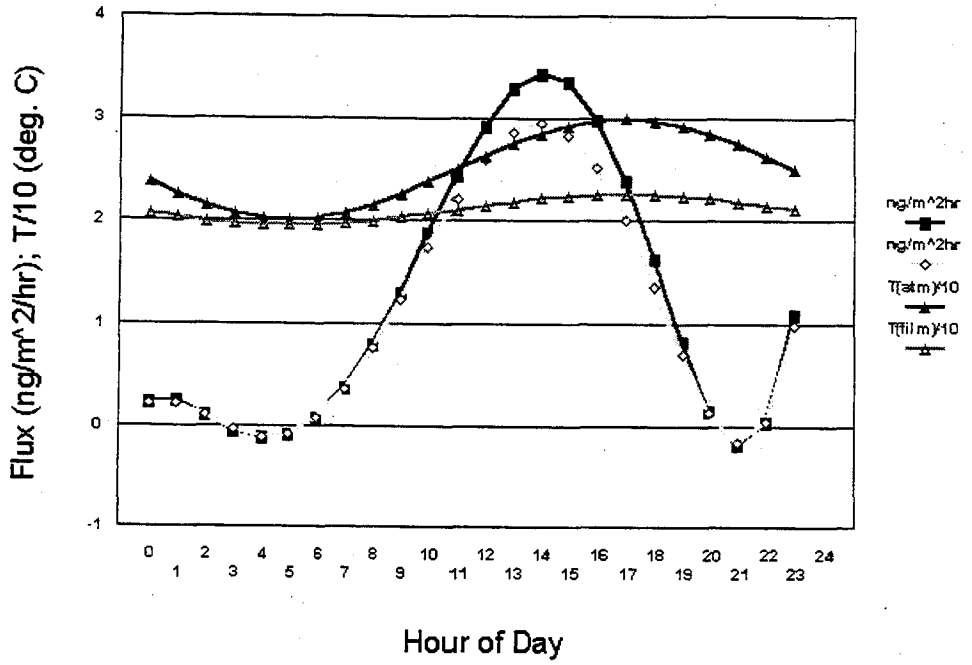

Figure 1. Comparison of simulated 24 hour wet and dry bulb atmospheric temperatures and simulated 24 hour estimated elemental mercury air-water exchange rates for data published by Krabbenhoft et al. (1998). Exchange simulations were conducted assuming that the temperature of the thin aqueous layer dominating elemental mercury air-water exchange rates equals either atmospheric wet or dry bulb thermometer values.

from their corresponding dry bulb values (i.e., the wet bulb temperature is traditionally measured at air flow rates [wind speeds] greater than circa 3 m/s); hence the true effect of evaporative cooling on air-water exchange rates is likely to be less under the quiescent conditions suitable for application of the two layer exchange model.

DISCLAIMER

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. EPA.

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